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Reduction of $Me_3SiCH_2AsCl_2$ (**I**) with $LiAlH_4$ at -78°C afforded $Me_3SiCH_2AsH_2$ (**II**), and reaction of **II** with Ph_3Ga produced $[Me_3SiCH_2(H)AsGaPh_2]_3$ (**III**) which was characterized by partial elemental analysis (C and H), ^1H NMR spectroscopy, and a cryoscopic molecular weight determination. Based on ^1H NMR data, $[Me_3SiCH_2(H)AsGaMe_2]_3$ (**IV**) was produced by the reaction of **II** with Me_3Ga; however, only H_2, Me_4Si, $(Me_3SiCH_2As)_5$ (**VI**), and unreacted $(Me_3SiCH_2)_3Ga$ were identified after allowing the latter to react with **II**. Reaction of two equivalents of Me_3SiCl with a mixture of **II** and *n*-BuLi (1:2 mole ratio) afforded $Me_3SiCH_2As(SiMe_3)_2$ (**V**). The monosilylated arsine was not isolated when one equivalent of Me_3SiCl was allowed to react with combined **II** and *n*-BuLi (1:1 mole ratio); rather, a mixture of **II** and **V** resulted. Attempted preparations of $(Me_3SiCH_2AsGaPh)_n$ are described. The ring compound $(Me_3SiCH_2As)_5$ (**VI**) was prepared by reaction of $Me_3SiCH_2AsCl_2$ with a mixture of Me_3SiCl and Mg in THF. (cont.)

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19. The molecular structure of this cycloarsane was determined by single-crystal X-ray diffraction methods. Pale yellow crystals of **VI** belong to the monoclinic system with four molecules occupying the general positions of space group $P2_1/c(C^5_{2h})$ with cell constants: a = 9.952(1), b = 30.245(9), c = 13.000(3) Å, β = 91.69(1)°, V = 3911.3 Å^3, Z = 4.

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Preparation and Chemistry of $Me_3SiCH_2AsH_2$; Preparation of $[Me_3SiCH_2(H)AsGaPh_2]_3$, A Trimeric Mono(Arsino)Gallane Containing A Hydrogen Bonded to Arsenic. Isolation and X-Ray Crystal Structure of $(Me_3SiCH_2As)_5$.

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PREPARATION AND CHEMISTRY OF $Me_3SiCH_2AsH_2$; PREPARATION OF $[Me_3SiCH_2(H)AsGaPh_2]_3$, A TRIMERIC MONO(ARSINO)GALLANE CONTAINING A HYDROGEN BONDED TO ARSENIC. ISOLATION AND X-RAY CRYSTAL STRUCTURE OF $(Me_3SiCH_2As)_5$.

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Abstract---Reduction of $Me_3SiCH_2AsCl_2$ (**I**) with $LiAlH_4$ at -78 °C afforded $Me_3SiCH_2AsH_2$ (**II**), and reaction of **II** with Ph_3Ga produced $[Me_3SiCH_2(H)AsGaPh_2]_3$ (**III**) which was characterized by partial elemental analysis (C and H), ^1H NMR spectroscopy, and a cryoscopic molecular weight determination. Based on ^1H NMR data, $[Me_3SiCH_2(H)AsGaMe_2]_3$ (**IV**) was produced by the reaction of **II** with Me_3Ga; however, only H_2, Me_4Si, $(Me_3SiCH_2As)_5$ (**VI**), and unreacted $(Me_3SiCH_2)_3Ga$ were identified after allowing the latter to react with **II**. Reaction of two equivalents of Me_3SiCl with a mixture of **II** and *n*-BuLi (1:2 mole ratio) afforded $Me_3SiCH_2As(SiMe_3)_2$ (**V**). The monosilylated arsine was not isolated when one equivalent of Me_3SiCl was allowed to react with combined **II** and *n*-BuLi (1:1 mole ratio); rather, a mixture of **II** and **V** resulted. Attempted preparations of $(Me_3SiCH_2AsGaPh)_n$ are described. The ring compound $(Me_3SiCH_2As)_5$ (**VI**) was prepared by reaction of $Me_3SiCH_2AsCl_2$ with a mixture of Me_3SiCl and Mg in THF. The molecular structure of this cycloarsane was determined by single-crystal X-ray diffraction methods. Pale yellow crystals of **VI** belong to the monoclinic system with four molecules occupying the general positions of space group $P2_1/c(C^5_{2h})$ with cell constants: $a = 9.952(1)$, $b = 30.245(9)$, $c = 13.000(3)$ Å, $\beta = 91.69(1)°$, $V = 3911.3$ Å^3, $Z = 4$.

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In recent years, after a hiatus of approximately two decades[1], there has been a considerable amount of activity in the area of gallium-arsenic chemistry[2], some of which was prompted by the search for new gallium arsenide precursors. As a result, a number of new and interesting compounds have been prepared and characterized. However, to date the literature contains no reports regarding the isolation and characterization of monomeric or oligomeric compounds of the type $[R(H)AsGaR'_2]_n$ and $(RAsGaR')_n$. As described by Coates and Beachley, the reactions of $MeAsH_2$ and $PhAsH_2$ with Me_3Ga gave only polymers[1b], whereas we found that the reaction of $PhAsH_2$ with $(Me_3SiCH_2)Ga$ gave a complex mixture of products from which $(PhAs)_6$ and the novel cluster $[(PhAsH)(R_2Ga)(PhAs)_6(RGa)_4]$ ($R = Me_3SiCH_2$) were isolated[2a].

Here we report the preparation of $Me_3SiCH_2AsCl_2$ (**I**) and its conversion to $Me_3SiCH_2AsH_2$ (**II**). Also, the reaction of **II** with Ph_3Ga to prepare $[Me_3SiCH_2(H)AsGaPh_2]_3$ (**III**), as well as some other reactions, including its conversion to $Me_3SiCH_2As(SiMe_3)_2$ (**V**) are described. In addition, attempts to prepare $(Me_3SiCH_2AsGaPh)_n$ are reported. Furthermore, we found that an attempted preparation of **V** from **II** resulted in the formation of the cycloarsane $(Me_3SiCH_2As)_5$, the crystal structure of which is described herein.

EXPERIMENTAL

General Information

All manipulations and reactions were carried out either in Schlenk apparatus, I[2]R glove bags, or a Vacuum/Atmospheres HE-43 Dri Lab under an inert atmosphere (argon or nitrogen), or on a vacuum line. Quantities of volatile products were measured on a vacuum line. Deionized water was degassed prior to use. All organic solvents were distilled from sodium benzophenone ketyl under nitrogen. $AsCl_3$, perfluorohexane, Me_3SiCH_2Cl, and Et_2NH were purchased from Strem Chemicals Inc., Specialty Chemicals, Petrarch Systems Inc., and EM Science, respectively. $LiAlH_4$, n-BuLi, and Me_3Ga were obtained from Alfa Products Inc. All commercially available reagents were not further purified. The concentration of the n-BuLi was determined each time before use by titration[3] with *sec*-BuOH in C_6H_6 using 1,10-phenanthroline as the indicator. Me_3SiCH_2MgCl was prepared in a 97% yield by a slight modification (i.e., baking the I_2 initiator and Mg metal turnings with a flame) of the literature method[4]. $(Et_2N)_2AsCl$[5], $PhGaCl_2$[6], Ph_2GaCl[7], Ph_3Ga[8], and $(Me_3SiCH_2)_3Ga$[9] were also prepared by literature methods. ^1H NMR spectra were recorded on either an IBM NR-80 spectrometer (80 MHz) or a Varian XL-300 (299.943 MHz), the latter being used to obtain variable temperature spectra. ^{13}C NMR spectra were obtained on either a JEOL FX-90Q spectrometer at 22.5 MHz or a Varian XL-300 spectrometer at 75.429 MHz. All spectra were referenced to TMS using the residual protons or the carbons of the deuterated solvents as the chemical shift reference; for ^{1}H, C_6D_5H δ 7.15, $C_6D_5CD_2H$ δ 2.09; for $^{13}C\{^{1}H\}$, C_6D_6 δ 128.0, $C_6D_5CD_3$ δ 20.4. All NMR tubes were flame-sealed under vacuum. A Normag 2029 apparatus was used to determine the molecular weight of **III** (cryscopically in cyclohexane). All melting point measurements were performed by using a Buchi 510 apparatus and flame-sealed capillaries. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, NY.

Syntheses

$Me_3SiCH_2AsCl_2$ (**I**)

Me_3SiCH_2MgCl (249 cm^3, 0.398 mol) was added dropwise with stirring to an Et_2O (300 cm^3) solution of $(Et_2N)_2AsCl$ (99.6 g, 0.391 mol) at -78 ^{o}C. An exothermic reaction occurred as the Grignard reagent was added dropwise. After stirring for 8 h at RT, the reaction mixture was hydrolyzed with a large excess of conc. HCl, and the organic layer was separated and combined with a hexane/Et_2O extract of the acid layer. Removal of solvents gave a yellow liquid (77.8 g) which was vacuum distilled to yield pure $Me_3SiCH_2AsCl_2$ as a colorless liquid (73.5 g, 81% yield, b.p. 30 ^{o}C/0.1-0.2 Torr). Anal. Calcd. for $C_4H_{11}AsCl_2Si$: C, 20.62; H, 4.76; Cl, 30.43. Found: C, 20.67; H, 4.70; Cl, 30.26. ^{1}H NMR (C_6D_6, 80.06 MHz): δ –0.070 (s, CH_3), 1.5 (s, CH_2).

$Me_3SiCH_2AsH_2$ (**II**)

To a stirred suspension of $LiAlH_4$ (6.68 g, 0.176 mol) in Et_2O (250 cm^3) at -78 ^{o}C was added dropwise a solution of **I** (20.5 g, 0.0880 mol) in Et_2O (50 cm^3). After the addition was complete, the mixture was hydrolyzed with a large excess of deionized water at 0 ^{o}C. A white solid [presumably $Al(OH)_3$ and LiOH] was separated from the mixture by filtration and washed with Et_2O. Addition of $MgSO_4$ to the separated organic layer, followed by filtration and removal of the solvent from the filtrate, afforded a yellow liquid which was vacuum distilled (30-40 ^{o}C/20-50 Torr) to give impure **II** as a colorless liquid. Purification was achieved by trap-to-trap fractionation, with pure **II** (6.81 g, 47.2% yield) being retained in a trap at -63 ^{o}C. Anal. Calcd. for $C_4H_{13}AsSi$: C, 29.27; H, 7.98. Found: C, 29.56, 29. 41; H, 8.03, 7.92. ^{1}H NMR (C_6D_6, 299.944

MHz): δ -0.021 (s, CH_3), 0.301 $^3J_{HH}$ = 7.44 Hz (t, CH_2), 2.054 (t, AsH_2). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.429 MHz): δ -5.425 (CH_2), -1.246 (CH_3).

Treatment of **I** with $LiAlH_4$ at RT afforded **II** in lower yield (25%), as well as some $(Me_3SiCH_2As)_5$ (**VI**).

$[Me_3SiCH_2(H)AsGaPh_2]_3$ (**III**)

1. Compound **II** (1.78 g, 10.8 mmol) and Ph_3Ga (3.26 g, 10.8 mmol) were combined in benzene (25 cm^3) and, after stirring the mixture overnight at 55-57 °C, the solvent was stripped off, leaving a colorless sticky residue. Volatiles were then removed *in vacuo* over a 4 day period to yield **III** as a less sticky material. Attempts to crystallize the product from C_6H_{14} or a mixture of ligroin and C_6F_{14} were unsuccessful. M.p. measurement: the colorless **III** became mobile at 57-59 °C, and it started to change to light yellow at 68 °C; it became a transparent liquid at 75-77 °C. Anal. Calcd. for $C_{48}H_{66}As_3Si_3Ga_3$: C, 49.65; H, 5.73. Found: C, 51.00, 51.05; H, 5.75, 5.77. Mol wt (0.303 g in 13.97 g of cyclohexane): Calcd. 1161; Found. 1172±23. ^1H NMR (C_6D_6, 299.944 MHz): δ -0.329, -0.332, -0.359 (3 s, CH_3), 0.768, 0.818, 0.882 $^3J_{HH}$ = 5.86, 5.88, 5.76 Hz (3 d, CH_2), 2.334, 2.451, 2.600 (3 t, AsH), 7.2-7.4 and 7.7-7.9 (m, Ph).

Reaction of Ph_3Ga (0.550 g, 1.83 mmol) with an excess of **II** (0.324 g, 1.97 mmol) yielded the same sticky product, with all Ph_3Ga being consumed. Drying the product under high vacuum for 5 days afforded colorless sticky **III** (0.708 g, 100% yield; ^1H NMR spectrum same as that of an authentic sample).

2. Slow addition of *n*-BuLi (1.56 cm^3, 2.34 mmol) to a stirred THF solution of **II** (0.384 g, 2.34 mmol) which was cooled in a -78 °C bath resulted in a slightly yellow solution. [Note: Treatment of **II** with n-BuLi in various solvents (hexane, ligroin, and THF) at RT, and even at 0 °C, resulted in a complex reaction mixture.] After stirring for 3 h, Ph_2GaCl (0.607 g, 2.34 mmol) was added by means of a side-arm dumper to the vessel. The bath was removed after stirring for another 3 h and the mixture was stirred for 1 h at RT, yielding a white solid (presumably LiCl). The mixture was filtered and washed with C_6H_6. Removal of solvents *in vacuo* from the filtrate afforded a yellow solid. The ^1H NMR spectrum of the latter revealed that **III** and an adduct of the gallium reactant [presumbly $Ph_2GaCl{\cdot}THF$] were present. Recrystallization of the yellow solid from hexane or a mixture of ligroin and THF provided light yellow crystals of the adduct.

$[Me_3SiCH_2(H)AsGaMe_2]_3$ (**IV**)

Me_3Ga (3.42 mmol), measured on a vacuum line, was condensed into a reaction vessel containing a pentane solution of **II** (0.551 g, 3.36 mmol) at -196 °C. The mixture was warmed to RT and stirred for 39 h. The evolved CH_4 (3.26 mmol) was measured, and volatiles were removed *in vacuo* leaving a mixture of a colorless liquid and a very small amount of a solid. A second experiment using Me_3Ga (1.80 mmol) with an excess of **II** (0.307 g, 1.87 mmol) gave a colorless mixture of a liquid and solid (0.400g, 84.6% yield) and CH_4 (1.45 mmol). The ^1H NMR spectra of both mixtures showed the same type of coupling pattern as that observed in the spectrum of **III**. ^1H NMR (C_6D_6, 299.944 MHz): δ 0.047 (s, Me_3Si); 0.206, 0.247, 0.294 (3 s, Me_2Ga); 0.785, 0.805, 0.823 $^3J_{HH}$ = 5.80 Hz (3 overlapping d, CH_2As); 1.697, 1.748, 1.790 (3 overlapping t, AsH).

Reaction of $Me_3SiCH_2AsH_2$ (**II**) with $(Me_3SiCH_2)_3Ga$

Compound **II** (0.25 g, 1.5 mmol) and $(Me_3SiCH_2)_3Ga$ (0.05 g, 1.5 mmol) were transferred into a 50 cm^3 bulb equipped with a Teflon stopcock and a magnetic stir bar. The bulb was attached to a vacuum line, cooled to -196 °C, and degassed. Stirring the mixture for a day at RT, followed by heating and stirring for 2 days at 51-63 °C, gave a yellow liquid, H_2 (1.2 mmol, 80% yield), and Me_4Si (0.21 mmol, 14% yield). After the liquid was transferred into a 50 cm^3 flask to which a solution of the remaining liquid and pentane used for rinsing the bulb was added, a few small particles [presumably unreacted $(Me_3SiCH_2)_3Ga$] were removed by filtration. Removal of the pentane *in vacuo* from the filtrate afforded a yellow liquid, the ^1H NMR spectrum of which revealed that **VI** and $(Me_3SiCH_2)_3Ga$ were present. The liquid residue was mixed with ligroin and perfluorohexane, and stored at -15 °C. A few months later, a crystal was isolated; its ^1H NMR spectrum showed a broad hump and many lines between δ 1.8 and -0.5.

$Me_3SiCH_2As(SiMe_3)_2$ (**V**)

To a stirred THF solution of **II** (1.171 g, 7.13 mmol) at -78 °C was slowly added *n*-BuLi (4.74 cm^3, 14.26 mmol). After stirring for 3 h, Me_3SiCl (1.8 cm^3, 14.28 mmol) was introduced into the mixture which turned colorless immediately after the addition. After stirring for another 3 h, the mixture was warmed to RT and stirred for 2 h. A white solid (presumably LiCl) was removed by filtration and washed with benzene. Volatiles were removed from the filtrate, and the liquid residue was distilled under vacuum to give **V** as a colorless liquid (1.82 g, 83% yield, b.p. 52-53 °C/0.1-0.2 Torr). Anal. Calcd. for

$C_{10}H_{29}AsSi_3$: C, 38.93; H, 9.47. Found: C, 38.72, 38.95; H, 9.55, 9.62. ^1H NMR (C_6D_6, 299.944 MHz): δ 0.177 (s, Me_3SiC), 0.254 (s, Me_3SiAs), 0.559 (s, CH_2). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.429 MHz): δ -5.690 (s, CH_2), -0.322 (s, Me_3SiC), 1.415 (s, Me_3SiAs).

Attempted Preparation of $Me_3SiCH_2As(H)SiMe_3$

n-BuLi (1.42 cm^3, 4.14 mmol) was added to a THF solution of **II** (0.680 g, 4.14 mmol) which was cooled with a -78 °C bath. After stirring for 3 h, Me_3SiCl (0.52 cm^3, 4.14 mmol) was added to the mixture. The bath was removed and the mixture was stirred for 3 h. A white solid (presumably LiCl) was separated by filtration and removal of solvents from the filtrate gave a liquid mixture of **II** and **V** (based on a ^1H NMR spectrum). Removal *in vacuo* of **II** from the mixture gave **V** (0.777 g, 61% yield).

When this reaction was repeated at RT, $(Me_3SiCH_2As)_5$ (**VI**), $(Me_3Si)_3As$, and an unidentified black precipitate were formed.

Attempted Preparation of $(Me_3SiCH_2AsGaPh)_n$

1. Heating **III** at 55-62 °C for 2 days in a Dri Lab produced a light yellow solid which on further heating at 76-82 °C for 2 days turned more yellow. The ^1H NMR spectrum of the yellow solid revealed that the coupling pattern of the trimer was collapsed, and a hump appeared at δ 0.5 to -0.5. Heating the yellow solid at 90-100 °C for another 2 days left the color unchanged, and a similar ^1H NMR spectrum was obtained (3 peaks at δ 3.106, 0.188, 0.128; two humps at δ 1.0 to 0.8 (small), 0.5 to -0.5 (larger, broad), and a shoulder at δ 2.4 to 1.0. M.p. measurement: the yellow solid turned brownish at 170 °C, red at 190 °C, and became a liquid at 210-225 °C. Anal. Calcd. for $C_{10}H_{16}SiAsGa$: C, 38.87; H, 5.22. Found: C, 40.44, 40.30; H, 5.41, 5.35.

2. *n*-BuLi (0.88 cm^3, 2.67 mmol) was added with stirring to an Et_2O solution of **II** (0.219 g, 1.34 mmol) in a reaction vessel which was immersed in a dry ice/acetone bath. After stirring for 1 h, $PhGaCl_2$ (0.292 g, 1.34 mmol) was added to the mixture by means of a side-arm dumper. The bath was removed 1 h later and precipitation of a white solid (presumably LiCl) was observed. The white solid (0.10 g, 88% yield) was removed by filtration and removal *in vacuo* of solvents from the filtrate gave a light yellow sticky residue. The ^1H NMR spectrum of the residue was relatively simple showing 1 peak at δ -0.024 and two broad humps between δ 2.0 and -0.5.

3. (a) A toluene solution of **V** (0.309 g, 1.00 mmol) was combined with a toluene solution of $PhGaCl_2$ (0.218 g, 1mmol) at -15 °C. After 18 h at -15 °C, followed by stirring for 27 h at RT, 1.36 equivalents of Me_3SiCl were formed. Heating for 13 h at 66 °C increased the amount of Me_3SiCl formed to 1.68 equivalents and afforded a

colorless sticky residue. Attempts to crystallize the product from hexane or ligroin were unsuccessful. The ^1H NMR spectrum of the residue was similar to that of the material obtained when **III** was decomposed at 80 °C (2 peaks at δ 2.104 and 0.294; 3 humps at δ 3.4 to 3.0, 2.0 to 1.0, and 0.5 to -0.5.

(b) After 12 h at -15 °C, a mixture similar to that described in (a) above was stirred for 4 days at RT and 1.53 equivalents of Me_3SiCl resulted. Alternating the reaction temperature between RT and -15 °C four times in 12 days, with removal of Me_3SiCl after each period, increased the total amount of Me_3SiCl formed to 1.79 equivalents. Removal of volatiles *in vacuo* afforded an off-white sticky residue. The ^1H NMR spectrum of the residue showed 2 peaks at δ 0.254 and 0.176, 3 humps at δ 2.3 to 1.1, 1.1 to 0.8, 0.5 to -0.5, and a small peak at δ 0.559.

$(Me_3SiCH_2As)_5$ (**VI**)

Compound **I** (15.0 g, 0.0644 mol) was slowly added to a THF solution of Me_3SiCl (120 cm^3) and Mg turnings (3.14 g, 0.129 mol). The resulting mixture was refluxed for 1 h and then stirred at RT for an additional 8 h.. Removal of volatiles *in vacuo* gave a mixture of an off-white solid and a yellow liquid which was filtered and washed with pentane. Removal of solvents from the filtrate afforded crude **VI** as a yellow liquid. Some of the diarsine $[(Me_3SiCH_2)_2As]_2$[2b] was produced during the attempted purification (distillation at 100-120 °C/0.1-0.2 Torr) of the crude product; but after a week at RT, pale yellow crystals of **VI** formed in the yellow distillate. The crystals (3.28 g, 31.4%; m.p. 47-48 °C) were removed mechanically from the liquid. Anal. Calcd. for $C_{20}H_{55}As_5Si_5$: C, 29.63; H, 6.84. Found: C, 29.61; H, 6.67. ^1H NMR (C_6D_6, 299.944 MHz): δ 0.185, 0.213, 0.219 (3 s, CH_3); 1.602 (s, CH_2); 1.515 and 1.738 $^2J_{HH}$ = 13.63 Hz, 1.538 and 1.687 $^2J_{HH}$ = 13.55 Hz (2 AB patterns, CH_2). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.429 MHz): δ 0.079, 0.266, 0.349 (3 s, CH_3); 8.145, 10.240, 12.736 (3 s, CH_2). The ^1H NMR spectrum of the remaining liquid showed the presence of the diarsine and **VI** (36%:64%, based on integral ratios). Total yield of **VI**: 5.53 g, 53%.

X-Ray Crystal Structure Determination

$(Me_3SiCH_2As)_5$ (**VI**)

All measurements were performed on an Enraf-Nonius CAD-4 diffractometer (Cu-*K*α radiation, λ = 1.5418 Å; incident-beam graphite monochromator; ω-2θ scans, θ_{max} = 67°). Unit-cell parameters were derived from the diffractometer setting angles for 25 reflections (40° < θ < 55°) widely separated in reciprocal space. Lorentz, polarization, and empirical absorption corrections were applied to the data. The crystal structure was solved by direct methods. Approximate positions for the non-hydrogen atoms were obtained from an *E*-map. Hydrogen atoms were included at their calculated positions in the final rounds of full-matrix least-squares refinement of non-hydrogen atom positional and anisotropic temperature factor parameters. Crystallographic calculations were performed on PDP11/44 and Micro Vax II computers by use of the Enraf-Nonius Structure Determination Package incorporating the direct methods program MULTAN11/82. Neutral atom scattering factors used in the structure-factor calculations were taken from *International Tables for X-Ray Crystallography*, vol. IV, The Kynoch Press, Birmingham, England, 1974. In the full-matrix least-squares iterations, $\Sigma w\Delta^2$ [$w = 1/\sigma^2(|F_o|)$, $\Delta = (|F_o| - |F_c|)$] was minimized. Further details of data collection and refinement are in Table 1. Bond lengths, bond angles, and torsion angles are listed in Table 2. Supplementary material: atomic coordinates, thermal parameters, bond lengths and angles, and crystal data have been deposited with the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

Syntheses and Reactions

Reduction of $Me_3SiCH_2AsCl_2$ (**I**), which was prepared according to eqs. 1-3, with $LiAlH_4$ in Et_2O at -78 °C afforded $Me_3SiCH_2AsH_2$ (**II**) (eq. 4). In contrast, the reduction at room temperature resulted in a significantly lower yield of **II**, as well as some of the cycloarsane $(Me_3SiCH_2As)_5$ (**VI**).

$$4Et_2NH + AsCl_3 \longrightarrow (Et_2N)_2AsCl + 2Et_2NH{\cdot}HCl \qquad (1)$$

$$(Et_2N)_2AsCl + Me_3SiCH_2MgCl \longrightarrow (Et_2N)_2AsCH_2SiMe_3 + MgCl_2 \qquad (2)$$

$$(Et_2N)_2AsCH_2SiMe_3 + 4HCl \longrightarrow \underset{\textbf{(I)}}{Me_3SiCH_2AsCl_2} + 2Et_2NH{\cdot}HCl \qquad (3)$$

$$2Me_3SiCH_2AsCl_2 + LiAlH_4 \longrightarrow \underset{\textbf{(II)}}{2Me_3SiCH_2AsH_2} + LiCl + AlCl_3 \qquad (4)$$

The reaction of primary arsine **II** with Ph_3Ga in benzene proceeded slowly at room temperature; however, the cleavage of a single Ga-C bond occurred quantitatively at 55-57 °C, yielding benzene and $[Me_3SiCH_2(H)AsGaPh_2]_3$ (**III**). This trimer was isolated as a colorless sticky material, and it did not eliminate benzene at room temperature. Monitoring of a sample of the reaction mixture between 43 and 80 °C by ^1H NMR spectroscopy revealed that the decomposition of the single cleavage product started at 58-60 °C and was completed at 80 °C. Efforts to crystallize **III** were not successful, but it could be characterized on the basis of molecular weight, ^1H NMR, and analytical data. It is interesting to note that whereas **III** is a trimer, $[(Me_3SiCH_2)_2AsGaPh_2]_2$ is a dimer[2c]. The ^1H NMR spectrum of **III** shows that two diastereoisomers exist depending on the disposition of As-H groups, *i.e.* axially or equatorially oriented on the $(Ga\text{-}As)_3$ ring. One isomer has three equivalent As-H protons, whereas the other has two equivalent As-H protons which are nonequivalent to the third As-H proton. It has been demonstrated by selective decoupling experiments that three different coupling patterns between the CH_2 protons and the As-H protons take place. In addition, reaction of $Me_3SiCH_2(H)AsLi$ with Ph_2GaCl afforded a yellow solid which, on the basis of its ^1H NMR spectrum contains **III**; however, recrystallization of the yellow solid did not yield **III**.

Reaction of **II** with Me_3Ga in pentane at room temperature also gave a single cleavage product which was isolated as a colorless liquid containing a small amount of solid that slowly melted/dissolved at room temperature. On the basis of its ^1H NMR spectrum, we believe this product is $[Me_3SiCH_2(H)AsGaMe_2]_3$ (**IV**). The spectrum shows the same coupling pattern as that exhibited in the spectrum of **III**, but three peaks for the Me_3Si protons are merged into one peak. The four peaks at δ 0.774, 0.795, 0.814, and 0.832 can be explained by overlapping of three doublets. Also, the three triplets for the As-H protons are partially overlapped. After storing this single cleavage product at -15 °C for nine weeks, it was observed that one of the three peaks in the NMR spectrum for the Me_2Ga protons was split into a doublet, and another one appeared to have some splitting. Also, two additional doublets and one singlet appeared in the methylene region, while one more multiplet appeared up-field adjacent to the three As-H triplets. These observations imply that the trimer (**IV**) underwent the loss of CH_4.

Only H_2, Me_4Si, **VI**, and unreacted $(Me_3SiCH_2)_3Ga$ were identified after allowing the latter to react with **II**. These results compare,in part, with those obtained by us in some related earlier work using the same tri(alkyl)gallane. Thus, with $PhAsH_2$, the products were H_2, Me_4Si, $(PhAs)_6$, and the cluster $[(PhAsH)(R_2Ga)(PhAs)_6(RGa)_4]$ (R = Me_3SiCH_2)[2a]; and with Ph_2AsH, the products were H_2, Me_4Si, $(Ph_2As)_2$, and impure $[Ph_2AsGa(CH_2SiMe_3)_2]_n$[2b]. On the other hand no side products were observed in the preparation of $[(Me_3SiCH_2)_2AsGaPh_2]_2$ from the reaction of $(Me_3SiCH_2)_2AsH$ with Ph_3Ga.[2c]

In a one-pot synthesis, $Me_3SiCH_2As(SiMe_3)_2$ (**V**) was obtained in a high yield from **II** *via* dilithiation followed by silylation at -78 °C. In contrast, efforts to isolate the monosilylated arsine, $Me_3SiCH_2As(H)SiMe_3$, were unsuccessful. Thus, using a procedure similar to that used to prepare **V**, afforded only **II** and **V.** It is reasonable to assume that, in fact, monosilylated **II** was formed at low temperature but, on warming to room temperature, it underwent disproportionation. When the entire procedure was repeated at room temperature, **VI**, $(Me_3Si)_3As$, and an unidentified black precipitate were formed.

Three approaches were utilized in attempts to prepare and isolate an oligomer of the type $(RAsGaR')_n$. First, compound **III** was slowly heated in an effort to eliminate one mole equivalent benzene. A ^{1}H NMR spectrum of a sample of **III** which had been heated for two days at 55-62 °C revealed that the elimination had started to occur, but **III** was still the predominant species. On subsequent heating for two days at 76-82 °C, a yellow solid formed, and its ^{1}H NMR spectrum contained broad peaks indicative of a polymer or mixture of oligomers/polymers. Although a completely "satisfactory elemental analysis" (C and H) was not obtained, the data strongly support a formulation of $(Me_3SiCH_2AsGaPh)_n$ for the yellow solid. Second, the reaction of $Me_3SiCH_2AsLi_2$ (prepared *in situ*) with $PhGaCl_2$ was investigated. There was also evidence in this case for the desired reaction product(s), but none was isolated in "pure" form. Third, dechlorosilylation reactions between **V** and $PhGaCl_2$ were carried out. In one experiment, a total of 1.68 equivalents of Me_3SiCl were evolved, leaving a colorless sticky residue. Attempts to crystallize the latter were unsuccessful; however, its ^{1}H NMR spectrum compares favorably to that obtained for the 80 °C decomposition product of **III**.

In an effort to prepare **V** by an alternate and more direct method, the reaction of **I** with a mixure of Me_3SiCl and Mg in THF was carried out. No evidence for the desired product **V** was obtained; rather, the reaction afforded $(Me_3SiCH_2As)_5$ (**VI**). This result conforms with the report that the reaction of *t*-$BuAsCl_2$ with Mg in THF or Et_2O yields $(t\text{-}BuAs)_5$, in addition to $(t\text{-}BuAs)_4$ and t-Bu_6As_8.[10] On the other hand, *t*-$BuP(SiMe_3)_2$ has been synthesized in high yield by the reaction of Me_3SiCl with Mg and *t*-$BuPCl_2$.[11] In the purification of **VI** by distillation *in vacuo*, a small amount of the diarsine $[(Me_3SiCH_2)_2As]_2$ was formed, and a mixture of the two products was obtained as a yellow liquid. After a week, **VI** crystallized from the liquid at room temperature, and single crystals suitable for an X-ray diffraction study were obtained.

Crystal Structure of $(Me_3SiCH_2As)_5$ *(VI)*

An ORTEP drawing of **VI** is shown in Figure 1. Crystallographic data and a summary of data collection and refinement are presented in Table 1, bond lengths, bond angles, and torsion angles are in Table 2, and a comparison of corresponding lengths and angles in **VI** and $(MeAs)_5$[12] is provided in Table 3. The As-As bond lengths are not all equal, As(1)-As(2) $\simeq$ As(2)-As(3) < As(3)-As(4) $\simeq$ As(4)-As(5) $\simeq$ As(5)-As(1), and their mean at 2.437 Å is slightly longer than that of 2.428 Å in $(MeAs)_5$ as is the mean As-C distance at 1.99 Å in **VI** *vs.* 1.96 Å in $(MeAs)_5$. Endocyclic torsion angles are related by an approximate C_s-symmetry axis passing through As(1) and the mid-point of the As(3)-As(4) bond, and thus the ring has an envelope-like conformation although it is clearly twisted somewhat as reflected in the distinctly non-zero value of 6.2° for the As(2)-As(3)-As(4)-As(5) torsion angle. As reflected in the values of corresponding torsion angles for **VI** and $(MeAs)_5$ (Table 3), the five-membered rings have similar conformations in both compounds.

NMR Spectra of $(Me_3SiCH_2As)_5$ *(VI)*

If the solid-state structure were to persist in solution, the ^1H NMR spectrum of **VI** would be expected to be very complex; however, it was found to be quite non-complex. It consisted of three singlets (intensity ratio 2:1:2)[13] [δ 0.185, 0.213, and 0.219 (CH_3)], two distinct AB patterns [δ 1.515 and 1.738, $^2J_{HH}$ = 13.63 Hz (CH_2); δ 1.538 and1.687, $^2J_{HH}$ = 13.55 Hz (CH_2)]. The $^{13}C\{^1H\}$ NMR spectrum of **VI** shows three singlets each for CH_3 and CH_2 carbons, proving that three types of Me_3SiCH_2 groups are present. In the presence of a symmetry-generating torsional (restricted pseudorotational) motion proposed by Rheingold[14], the symmetrical intermediate of **VI** would give exactly the same resonances as shown in the ^1H NMR spectrum which was obtained. The steric restrictions imposed by bulky Me_3SiCH_2 groups has a dampening effect on pseudorotation[15] of the ring puckering. As a result, a limited pseudorotation responsible for a time-averaged plane of symmetry takes place. According to Rheingold, there are four possible inversional isomers for the five-membered ring in $(ClCH_2As)_5$[14]. Interestingly, compound **VI** in the solid state has the conformation which corresponds to that isomer with the lowest internal energy.

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Table 1. Crystallographic data and summary of data collection and refinement[a] for $(Me_3SiCH_2As)_5$ (VI)

Formula	$C_{20}H_{55}As_5Si_5$
Formula weight	810.70
Crystal system	Monoclinic
Space group	$P2_1/c(C^5_{2h})$
Conditions	$0k0$, $k = 2n$; $h0l$, $l = 2n$
Crystal dimensins, mm	0.20 x 0.30 x 0.30
Crystal color and habit	Pale yellow prisms
Temperature, K	298
a, Å	9.952(1)
b, Å	30.245(9)
c, Å	13.000(3)
β, deg	91.69(1)
Z	4
V, $Å^3$	3911.3
d_{calcd}, g cm^{-3}	1.377
Linear absorption coefficient, cm^{-1}	65.5
Scan speed, deg min^{-1}	Variable
Scan width, deg	$1.20 + 0.14\tan\theta$
Max θ, deg	67
Background	25% additional scan at each end of scan
Range of absorbance factors	0.48-1.00
Octants	$+h$, $+k$, $\pm l$
Number of variables	272
Data/variable ratio	13.8
Check reflections	(1, 4, 2), (1, 4, 2)
Decay of standards	< 1%
Number of reflections collected	7226
R(merge)	0.033 on I, 0.024 on $\lvert F_o \rvert$
Number of unique data	6919
Number of data used in refinement	3744 [$I > 3.0\sigma(I)$]

Table 1. (continued)

R(F)	0.037
R_w(F)	0.049
Extinction coefficient	9.5×10^{-8}
Weighting scheme, ω	$1/\sigma^2 (\|F_o\|)$
E. s. d. of an observation of unit weight	1.22
Largest Δ/σ	0.06
Largest feature of final diff map, e $Å^{-3}$	0.53
Location of feature	1.4 Å from As(3) and As(4)

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ with weighting scheme as listed above.

Table 2. Bond Lengths (Å), bond angles (deg), and torsion angles (Å), with estimated standard deviations in parentheses, for $(Me_3SiCH_2As)_5$ (VI)

Deviations in Parentheses

(a) Bond Lengths

As(1)-As(2)	2.428(1)	Si(2)-C(22)	1.847(13)
As(1)-As(5)	2.443(1)	Si(2)-C(23)	1.867(13)
As(1)-C(11)	1.992(6)	Si(2)-C(24)	1.866(12)
As(2)-As(3)	2.424(1)	Si(3)-C(31)	1.870(6)
As(2)-C(21)	1.987(7)	Si(3)-C(32)	1.871(10)
As(3)-As(4)	2.443(1)	Si(3)-C(33)	1.857(10)
As(3)-C(31)	2.014(7)	Si(3)-C(34)	1.865(11)
As(4)-As(5)	2.446(1)	Si(4)-C(41)	1.861(9)
As(4)-C(41)	1.978(8)	Si(4)-C(42)	1.855(10)
As(5)-C(51)	1.995(7)	Si(4)-C(43)	1.840(13)
Si(1)-C(11)	1.861(7)	Si(4)-C(44)	1.853(11)
Si(1)-C(12)	1.847(11)	Si(5)-C(51)	1.889(8)
Si(1)-C(13)	1.849(11)	Si(5)-C(52)	1.865(12)
Si(1)-C(14)	1.876(10)	Si(5)-C(53)	1.873(11)
Si(2)-C(21)	1.867(8)	Si(5)-C(54)	1.864(12)

(b) Bond Angles

As(2)-As(1)-As(5)	99.05(4)	C(22)-Si(2)-C(24)	109.1(6)
As(2)-As(1)-C(11)	97.2(2)	C(23)-Si(2)-C(24)	105.8(5)
As(5)-As(1)-C(11)	99.4(2)	C(31)-Si(3)-C(32)	111.6(4)
As(1)-As(2)-As(3)	96.46(4)	C(31)-Si(3)-C(33)	110.3(4)
As(1)-As(2)-C(21)	104.3(2)	C(31)-Si(3)-C(34)	106.4(4)
As(3)-As(2)-C(21)	101.2(2)	C(32)-Si(3)-C(33)	107.3(5)

Table 2. (continued)

As(2)-As(3)-As(4)	105.24(4)	C(32)-Si(3)-C(34)	109.7(5)
As(2)-As(3)-C(31)	94.3(2)	C(33)-Si(3)-C(34)	111.6(5)
As(4)-As(3)-C(31)	98.6(2)	C(41)-Si(4)-C(42)	111.2(4)
As(3)-As(4)-As(5)	104.59(4)	C(41)-Si(4)-C(43)	108.6(5)
As(3)-As(4)-C(41)	96.9(2)	C(41)-Si(4)-C(44)	108.7(5)
As(5)-As(4)-C(41)	96.9(3)	C(42)-Si(4)-C(43)	108.8(5)
As(1)-As(5)-As(4)	98.29(4)	C(42)-Si(4)-C(44)	108.9(5)
As(1)-As(5)-C(51)	96.8(2)	C(43)-Si(4)-C(44)	110.7(5)
As(4)-As(5)-C(51)	95.9(2)	C(51)-Si(5)-C(52)	109.6(4)
C(11)-Si(1)-C(12)	110.7(5)	C(51)-Si(5)-C(53)	107.1(4)
C(11)-Si(1)-C(13)	110.4(4)	C(51)-Si(5)-C(54)	111.9(4)
C(11)-Si(1)-C(14)	107.1(4)	C(52)-Si(5)-C(53)	109.0(6)
C(12)-Si(1)-C(13)	109.2(5)	C(52)-Si(5)-C(54)	110.2(5)
C(12)-Si(1)-C(14)	108.7(5)	C(53)-Si(5)-C(54)	109.1(5)
C(13)-Si(1)-C(14)	110.8(5)	As(1)-C(11)-Si(1)	116.1(3)
C(21)-Si(2)-C(22)	109.1(5)	As(2)-C(21)-Si(2)	115.3(4)
C(21)-Si(2)-C(23)	112.3(4)	As(3)-C(31)-Si(3)	114.0(4)
C(21)-Si(2)-C(24)	111.3(4)	As(4)-C(41)-Si(4)	116.6(5)
C(22)-Si(2)-C(23)	109.0(8)	As(5)-C(51)-Si(5)	112.3(3)
(c) Torsion Angles[a]			
As(5)-As(1)-As(2)-As(3)	57.91(4)	As(3)-As(4)-As(5)-C(51)	126.8(2)
As(5)-As(1)-As(2)-C(21)	-45.4(2)	C(41)-As(4)-As(5)-As(1)	128.1(2)
C(11)-As(1)-As(2)-As(3)	158.7(2)	C(41)-As(4)-As(5)-C(51)	-134.1(3)
C(11)-As(1)-As(2)-C(21)	55.4(3)	As(3)-As(4)-C(41)-Si(4)	-92.7(4)
As(2)-As(1)-As(5)-As(4)	-54.46(4)	As(5)-As(4)-C(41)-Si(4)	161.6(4)

Table 2. (continued)

As(2)-As(1)-As(5)-C(51)	-151.4(2)	As(1)-As(5)-C(51)-Si(5)	-169.3(3)
C(11)-As(1)-As(5)-As(4)	-153.4(2)	As(4)-As(5)-C(51)-Si(5)	91.6(3)
C(11)-As(1)-As(5)-C(51)	109.7(3)	C(12)-Si(1)-C(11)-As(1)	79.3(5)
As(2)-As(1)-C(11)-Si(1)	174.3(4)	C(13)-Si(1)-C(11)-As(1)	-41.8(6)
As(5)-As(1)-C(11)-Si(1)	-85.3(4)	C(14)-Si(1)-C(11)-As(1)	-162.4(5)
As(1)-As(2)-As(3)-As(4)	-38.89(4)	C(22)-Si(2)-C(21)-As(2)	150.0(7)
As(1)-As(2)-As(3)-C(31)	61.2(2)	C(23)-Si(2)-C(21)-As(2)	29.0(7)
C(21)-As(2)-As(3)-As(4)	67.1(2)	C(24)-Si(2)-C(21)-As(2)	-89.5(6)
C(21)-As(2)-As(3)-C(31)	167.2(3)	C(32)-Si(3)-C(31)-As(3)	70.0(6)
As(1)-As(2)-C(21)-Si(2)	178.3(3)	C(33)-Si(3)-C(31)-As(3)	-49.2(5)
As(3)-As(2)-C(21)-Si(2)	78.6(4)	C(34)-Si(3)-C(31)-As(3)	-170.4(5)
As(2)-As(3)-As(4)-As(5)	6.16(5)	C(42)-Si(4)-C(41)-As(4)	45.8(6)
As(2)-As(3)-As(4)-C(41)	-92.9(3)	C(43)-Si(4)-C(41)-As(4)	165.5(5)
C(31)-As(3)-As(4)-As(5)	-90.7(2)	C(44)-Si(4)-C(41)-As(4)	-74.1(6)
C(31)-As(3)-As(4)-C(41)	170.3(3)	C(52)-Si(5)-C(51)-As(5)	58.5(5)
As(2)-As(3)-C(31)-Si(3)	160.3(3)	C(53)-Si(5)-C(51)-As(5)	176.5(4)
As(4)-As(3)-C(31)-Si(3)	-93.6(3)	C(54)-Si(5)-C(51)-As(5)	-64.0(5)
As(3)-As(4)-As(5)-As(1)	29.05(4)		

[a]The torsion angle A-B-C-D is defined as positive if, when viewed along the B-C bond, atom A must be rotated clockwise to eclipse atom D.

Table 3. Comparison of bond lengths (Å) and angles (deg) in $(MeAs)_5$[a] and $(MeSiCH_2As)_5$ (VI)

	$(MeAs)_5$	$[Me_3SiCH_2As]_5$
Bond lengths		
As(1)-As(2)	2.422(5)	2.428(1)
As(1)-As(5)	2.441(5)	2.443(1)
As(2)-As(3)	2.419(5)	2.424(1)
As(3)-As(4)	2.429(4)	2.443(1)
As(4)-As(5)	2.430(5)	2.446(1)
Bond Angles		
As(2)-As(1)-As(5)	100.4(2)	99.05(4)
As(1)-As(2)-As(3)	97.5(2)	96.46(4)
As(2)-As(3)-As(4)	105.4(2)	105.24(4)
As(3)-As(4)-As(5)	105.4(2)	104.59(4)
As(1)-As(5)-As(4)	100.0(2)	98.29(4)
Torsion Angles		
As(5)-As(1)-As(2)-As(3)	54.6(2)	57.91(4)
As(1)-As(2)-As(3)-As(4)	-38.8(2)	-38.89(4)
As(2)-As(3)-As(4)-As(5)	9.1(2)	6.16(5)
As(3)-As(4)-As(5)-As(1)	24.4(2)	29.05(4)
As(4)-As(5)-As(1)-As(2)	-49.4(2)	-54.46(4)

[a]The bond length and bond angle values for $(MeAs)_5$ were calculated using positional parameters contained in reference 12.

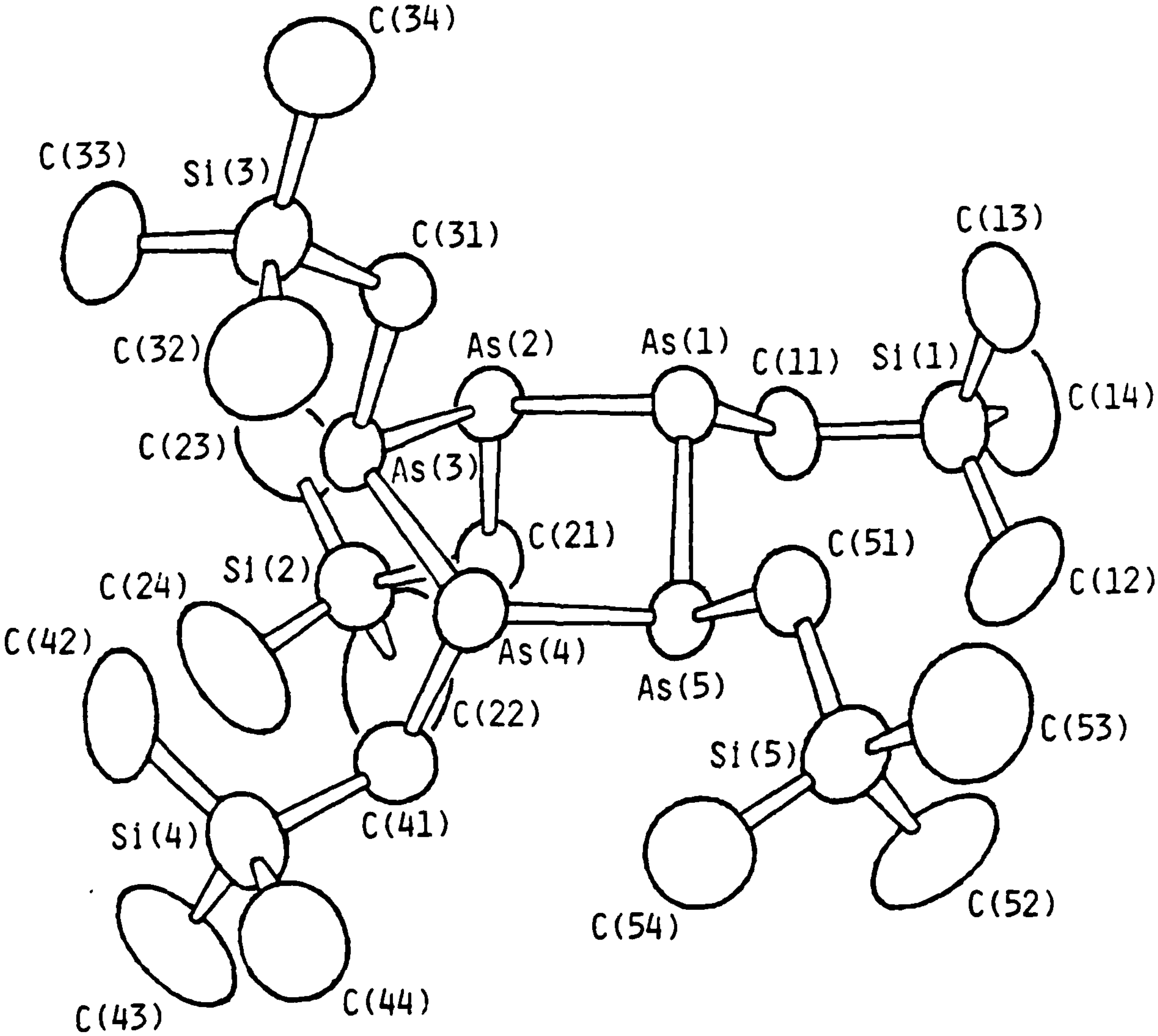

Figure 1. ORTEP drawing of $(Me_3SiCH_2As)_5$ (VI); hydrogen atoms are omitted for clarity.

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